Spin-orbital physics for p orbitals in alkali $R\mathrm{O}_2$ hyperoxides — Generalization of the Goodenough-Kanamori rules

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Abstract. - We derive a realistic spin-orbital model at finite Hund's exchange for alkali hyperoxides. We find that, due to the geometric frustration of the oxygen lattice spin and orbital waves destabilize both spin and p-orbital order in almost all potential ground states. We show that the orbital order induced by the lattice overrules the one favoured by superexchange and that this, together with the large interorbital hopping, leads to generalized Goodenough-Kanamori rules. They (i) lift the geometric frustration of the lattice, and (ii) explain the observed layered C-type antiferromagnetic order in alkali hyperoxides. This is confirmed by a spin-wave dispersion with no soft-mode behavior presented here as a prediction for future experiments.

Alkali $R\mathrm{O}_2$ (with R=K,Rb,Cs) hyperoxides attracted a lot of attention in the 70s and 80s [1] but then have been overshadowed by various classes of transition metal oxides — largely due to the discovery of the high temperature superconductivity and colossal magnetoresistance in the latter. These and other fascinating phenomena arise in transition metal oxides due to strong local Coulomb correlations within party filled d orbitals [2]. A particular class of these compounds are systems with orbital degeneracy in which the effective low-energy interactions involve not only spin but also orbital degrees of freedom within the spin-orbital superexchange [3, 4]. One of its consequences are rather complex phase diagrams in doped manganites [5] that follow from competing magnetic interactions in unfrustrated perovskite lattice. These systems are of great interest at present because orbital superexchange interactions are directional and thus intrinsically frustrated [6]. Following this idea, purely orbital frustrated models were developed and serve as paradigmatic models for investigating order-disorder phenomena and quantum phase transitions [7–9]. On one hand, such interactions are usually inherently coupled to spin interactions and such exotic phenomena as joint spin-orbital excitations [6] or entangled states [10] arise. On the other hand, they also couple to lattice distortions that may remove frustration and stabilize magnetic order [11–15].

Quite recently, it was realized that spin-orbital physics with p orbitals determines the physical properties of $R\mathrm{O}_2$ hyperoxides [16–19]. While an independent-electron picture suggests that the $R\mathrm{O}_2$ hyperoxides are FM halfmetals, they are in fact Mott insulators with one hole shared between the two antibonding O_2 molecular p orbitals [16]. Thus the localized hole has an orbital p degree of freedom (in addition to spin). Along with solid oxygen [20], the alkali hyperoxides constitute one of the few examples of defect-free p-band Mott insulators in condensed matter systems [16, 17]: thus they share certain common features of the above mentioned transition metal oxides with $3d$ electrons, and with the novel p-orbital systems in optical lattices [21–24]. Yet, despite the recent interest in these compounds, a central question concerning their properties has not been answered: what is the origin of the same magnetic order observed in the $R\mathrm{O}_2$ hyperoxides below a Néel temperature that varies between 5 to 15 K [1]? As we show below, the antiferromagnetic (AF) order is here indeed due to a different mechanism than the ones usually discussed in transition metal oxides [2], namely a frustration between lattice-driven and correlation-driven effects.

A 'perfect' AF order, with opposite spins along all nearest-neighbour bonds, is excluded in the frustrated body centered tetragonal (bct) lattice common for all alkali hyperoxides, see Fig. 1(a). The observed magnetic

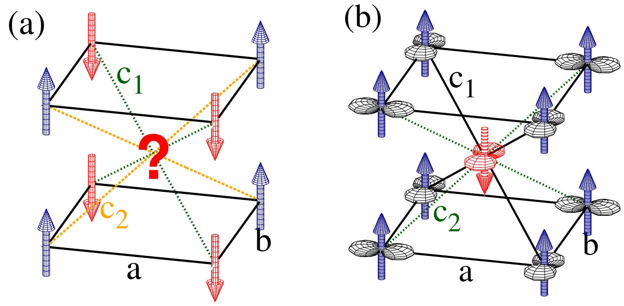

Fig. 1: (Colour on-line) (a): Spin Heisenberg model on the bct lattice is frustrated. (b): Yet, a layered C-AF spin order is stable in alkali RO_2 hyperoxides [1]. Orbital ordering might explain it, though a violation of Goodenough-Kanamori rules is inevitable in at least one plane (here shown along the dotted c_2 bonds), see text.

order is instead a layered C-type antiferromagnetic (C-AF) order, with ferromagnetic (FM) ab planes and AF c_1 and c_2 bonds, shown in Fig. 1(b). As we discuss in more detail below, the geometric frustration continues to play here a fundamental role via the Goodenough-Kanamori rules (GKR) [25] and tends to destabilize the C-AF order as well. It turns out that the observed magnetic order can only arise when the well-established (classical) GKR are not obeyed and they are replaced by *generalized* GKR. We show that the competition between superexchange and a generic Jahn-Teller (JT) effect leads to an orbital pattern with substantial interorbital hopping and that this in turn induces the generalized GKR driving the C-type AF order. The experimentally observed magnetic order thus arises from rather subtle interplay between spin-orbital physics and orbital-lattice coupling present in the alkali hyperoxides, being strikingly different from both d-orbital physics in transition metal oxides, and also from the p-orbital optical lattices.

First we show that geometric frustration is incompatible with the GKR , which state [25] that a bond with alternating orbital (AO) order leads to FM spin exchange, while ferro-orbital (FO) order induces AF spin coupling. A C-type AF order can thus arise if bonds within the FM ab plane show AO order, and those in the AF c directions should show FO order. In many transition metal oxides, such coexisting spin-orbital order arises, e.g., in the archetypal orbital system $KCuF_3$ [3]. However, this mechanism is here frustrated due to the bct lattice geometry, in a similar manner as the 'perfectly' AF state depicted in Fig. 1(a) — the experimentally found FM order within the planes requires AO order along a and b bonds. In the next higher plane along the c direction, see the shaded orbital and spin in Fig. 1(b), either choice of the orbital leads to some bonds with AO order and other bonds with FO order. Consequently, the GKR would imply FM spin exchange either along c_2 [as in Fig. 1(b)] or along c_1, while the observed order is AF along both c_1 and c_2. The C-type AF order thus violates the GKR due to geometric frustration on the bct lattice.

Since the magnetic order is AF along c_2 bonds, the effective FM magnetic interaction predicted by the GKR would have the 'wrong' sign. Such frustrated 'wrong' couplings can in principle still be compatible with long-range order — cf. a $J_1 - J_2$ model on a square lattice [26] or if the GKR violation is driven by spin-orbital entanglement [10]. But we show below that in the present case, the 'wrong' signs lead to soft modes in magnetic and orbital excitations which destroy long-range order — this phenomenon is somewhat similar to the collapse of order due to enhanced quantum fluctuations in coupled spin-orbital systems [6]. The geometric frustration in the bct lattice thus not only leads to violation of the GKR, but also destabilizes magnetic order whenever these rules are violated. We are going to show that the 'way out' suggested by the alkali hyperoxides are the generalized GKR explained below.

In the Mott-insulating limit of strong intraorbital Coulomb repulsion U applicable to RO_2 [16, 19], the interacting spin and p-orbital degrees of freedom can be described by a spin-orbital Hamiltonian. In an orbital basis given by the p_x and p_y orbital, one finds the superexchange Hamiltonian for finite Hund's exchange $\eta \equiv J_H/U$

$$\mathcal{H} = \sum_{\langle\mathbf{ij}\rangle||\gamma} \left\{ \hat{J}^{\gamma}_{\mathbf{ij}} \left(\mathbf{S_i}\cdot\mathbf{S_j}\right) + \hat{K}^{\gamma}_{\mathbf{ij}} \right\}, \qquad (1)$$

where $\gamma \in \{ab, c_1, c_2\}$ denotes the bond direction and the orbital operators modulating the magnetic exchange are:

$$\begin{aligned}
\hat{J}^{ab}_{\mathbf{ij}}/J_\sigma &= \alpha\left(r_{13}T^x_{\mathbf{i}}T^x_{\mathbf{j}} + r_{12\bar{3}}T^y_{\mathbf{i}}T^y_{\mathbf{j}}\right) \\
&+ \frac{1+\alpha^2}{2}\left(r_{13}T^z_{\mathbf{i}}T^z_{\mathbf{j}} - \frac{r_{1\bar{2}\bar{3}}}{4}\right), \qquad (2)\\
\hat{K}^{ab}_{\mathbf{ij}}/J_\sigma &= \frac{1}{4}\alpha\left(R_{1\bar{3}}T^x_{\mathbf{i}}T^x_{\mathbf{j}} + R_{1\bar{2}\bar{3}}T^y_{\mathbf{i}}T^y_{\mathbf{j}}\right) \\
&+ \frac{1+\alpha^2}{8}R_{1\bar{3}}T^z_{\mathbf{i}}T^z_{\mathbf{j}}, \qquad (3)\\
\hat{J}^{c1,c2}_{\mathbf{ij}}/J_{xx} &= (1+\beta^2)\left(r_{13}T^x_{\mathbf{i}}T^x_{\mathbf{j}} - \frac{r_{1\bar{2}\bar{3}}}{4}\right) \\
&\pm \beta r_{23}(T^x_{\mathbf{i}} + T^x_{\mathbf{j}}) \\
&+ (1-\beta^2)\left(r_{12\bar{3}}T^y_{\mathbf{i}}T^y_{\mathbf{j}} + r_{13}T^z_{\mathbf{i}}T^z_{\mathbf{j}}\right), \qquad (4)\\
\hat{K}^{c1,c2}_{\mathbf{ij}}/J_{xx} &= \frac{1}{4}(1+\beta^2)R_{1\bar{3}}T^x_{\mathbf{i}}T^x_{\mathbf{j}} \mp \frac{1}{4}\beta r_{23}(T^x_{\mathbf{i}} + T^x_{\mathbf{j}}) \\
&+ \frac{1}{4}(1-\beta^2)\left(R_{1\bar{2}\bar{3}}T^y_{\mathbf{i}}T^y_{\mathbf{j}} + R_{1\bar{3}}T^z_{\mathbf{i}}T^z_{\mathbf{j}}\right). \qquad (5)
\end{aligned}$$

Here $\mathbf{S_i}$ are spin $S = 1/2$ operators, and $\mathbf{T_i} \equiv \{T^x_{\mathbf{i}}, T^x_{\mathbf{i}}, T^z_{\mathbf{i}}\}$ are $T = 1/2$ orbital pseudospin operators for p orbitals $a(b)$ (see footnote [1]), with electron number operators $\{n_{\mathbf{i}a}, n_{\mathbf{i}b}\}$, and $T^z_{\mathbf{i}} = (n_{\mathbf{i}a} - n_{\mathbf{i}b})/2$. Although interorbital hopping within the ab plane vanishes in the chosen orbital basis $\{p_x, p_y\}$, different longitudinal (t_σ) and

[1] For simplicity we neglect a small superexchange term which is different along a and b direction; we have verified that it does not lead to distinct results.

transverse (t_π) hoppings lead to rather involved superexchange terms: Ising terms $\propto J_\sigma = 4t_\sigma^2/U$ and $\propto \alpha^2 J_\sigma$ and 'quantum' terms $\propto \alpha J_\sigma$, where $\alpha \equiv t_\pi/t_\sigma$. On the other hand, between the ab planes (i.e., in the c_1 and c_2 planes) the diagonal hoppings t_{xx} between each pair of the same molecular orbitals aa or bb result in superexchange $\propto J_{xx} = 4t_{xx}^2/U$. This is furthermore accompanied by a substantial interorbital hopping t_{xy} (see below), leading to additional superexchange channels $\propto \beta J_{xx}$ and $\propto \beta^2 J_{xx}$, with $\beta \equiv t_{xy}/t_{xx}$ and the $\pm$ signs corresponding to (111) and ($1\bar{1}1$) directions. Hund's exchange contributes via: $r_{13} = r_1 + r_3$, $r_{23} = r_2 + r_3$, $r_{12\bar{3}} = r_1 + 2r_2 - r_3$, $r_{1\bar{2}\bar{3}} = r_1 - 2r_2 - r_3$, $R_{1\bar{3}} = 3r_1 - r_3$, $R_{1\bar{2}3} = 3r_1 - 2r_2 + r_3$, where $r_1 = 1/(1-3\eta)$, $r_2 = 1/(1-\eta)$ and $r_3 = 1/(1+\eta)$.

In what follows we take the units of $J_\sigma \equiv 1$ and assume a realistic value of $\eta = 0.15$ [16,18] and $J_{xx}/J_\sigma = 0.4$ [19]. We have verified that small changes of these two latter parameters (possible for different RO_2) do not change the main results of the paper. However, we vary the transverse hopping α and interorbital hopping β, since the phase diagram of the spin-orbital Hamiltonian Eq. (1) shows quite distinct behaviour for different parameter regimes. Investigating various regimes will thus turn out to be illustrative, as different processes are dominant in each. Based on recent studies which predicted $(\alpha,\beta) = (0.01, 1.90)$ for KO_2 [16] and $(\alpha,\beta) = (0.30, 1.77)$ for RbO_2 [19] we suggest that a *realistic* parameter range for these hoppings in RO_2 is $\alpha \in [0.0, 0.3]$ and $\beta \in [1.5, 2.0]$.

We obtained the classical energies of a large variety of candidate ground states with at most two sublattices (Monte-Carlo simulations of the classical model did not indicate larger unit cells). Since the orbital interactions are not SU(2) symmetric, it has to be established whether orbital order involves T^x or T^z pseudospins. We have verified that the orbital order of T^y pseudospins is destabilized by orbital waves, similar to the spin-wave case discussed in more detail below, for any realistic parameters and it is thus enough to consider only T^x or T^z orbital order (we omit here a 'canted' phase with pseudospin in the xz plane) [27] (see also footnote [2]). The large degeneracy reported in Ref. [19] for $\eta = 0$ is partly removed by finite Hund's exchange $\eta > 0$ which splits off the energies of intermediate p^2 states and favours more some superexchange processes. Still several classical states are very close in energy — indeed this feature is generic for frustrated spin-orbital interactions near orbital degeneracy [6].

Via a mean-field decoupling (justified here due to large η, cf. Ref. [10]), a given orbital order yields an effective Heisenberg Hamiltonian for the spins:

$$H_{\rm S} = J_{ab} \sum_{\langle \mathbf{ij} \rangle || ab} \mathbf{S_i}\cdot\mathbf{S_j} + J_{c1} \sum_{\langle \mathbf{ij} \rangle || c1} \mathbf{S_i}\cdot\mathbf{S_j} + J_{c2} \sum_{\langle \mathbf{ij} \rangle || c2} \mathbf{S_i}\cdot\mathbf{S_j}, \quad (6)$$

where $\{J_{ab}, J_{c1}, J_{c2}\}$ are the effective magnetic exchange

[2] The classical Monte Carlo did likewise not indicate any T^y order.

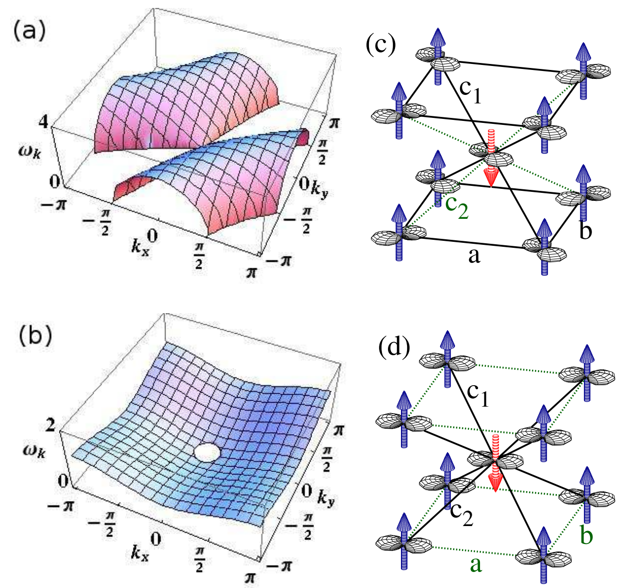

Fig. 2: (Colour on-line) Collapse of spin order in the LSWT [(a,b): soft modes in $\omega_{\mathbf{k}}$ at $k_z = 0$] for two representative orbital states: (a,c) — C-AOx order may explain the FM order in the ab plane according to GKR [solid bonds in (c)] but spin exchanges in the $c2$ plane have wrong signs [dashed bonds in (c)]. (b,d) — FOz order stabilizes the AF order in the $\{c_1, c_2\}$ planes according to GKR [solid bonds in (d)], but gives wrong signs of spin exchanges in the ab planes [dashed bonds in (d)]. Parameters: $\alpha = 0.30$ and $\beta = 1.77$ [19].

constants determined from the spin-orbital model [10],

$$J_\gamma(\phi) \equiv \langle \phi | \hat{J}^\gamma_{\mathbf{ij}} | \phi \rangle, \quad (7)$$

$\gamma = ab, c_1, c_2$ and $|\phi\rangle$ is the orbital ground state. By assuming classical C-AF order and determining quantum corrections via the linear spin-wave theory (LSWT), we now show that the frustration has a decisive impact on the ground state.

Using Holstein-Primakoff bosons $\alpha^\dagger_{\mathbf{k}}$, after Fourier and Bogoliubov transformations one obtains from Eq. (6),

$$H_{\rm S} = \sum_{\mathbf{k}} \omega_{\mathbf{k}} \left(\alpha^\dagger_{\mathbf{k}} \alpha_{\mathbf{k}} + \frac{1}{2} \right), \quad (8)$$

with the spin-wave dispersion

$$\omega_{\mathbf{k}} = \sqrt{A_{\mathbf{k}}^2 - B_{\mathbf{k}}^2}\,, \quad (9)$$

$A_{\mathbf{k}} = 2\{J_{ab}(\gamma_{\mathbf{k}} - 1) + J_{c1} + J_{c2}\}$, and $B_{\mathbf{k}} = 2(J_{c1}\eta_{\mathbf{k}} + J_{c2}\zeta_{\mathbf{k}})$. Here $\gamma_{\mathbf{k}} = (\cos k_x + \cos k_y)/2$, $\eta_{\mathbf{k}} = \cos(k_x/2 - k_y/2)\cos(k_z/2)$ and $\zeta_{\mathbf{k}} = \cos(k_x/2 + k_y/2)\cos(k_z/2)$ follow from the bct lattice structure. As can be seen in Figs. 2(a) and 2(b) for two representative orbital states $|\phi\rangle$ (see also below), $A_{\mathbf{k}}^2 < B_{\mathbf{k}}^2$ in parts of the Brillouin zone. This happens when any of the inequalities $J_{ab} < 0$, $J_{c1} > 0$, $J_{c2} > 0$ is not fulfilled (giving rise to the above mentioned

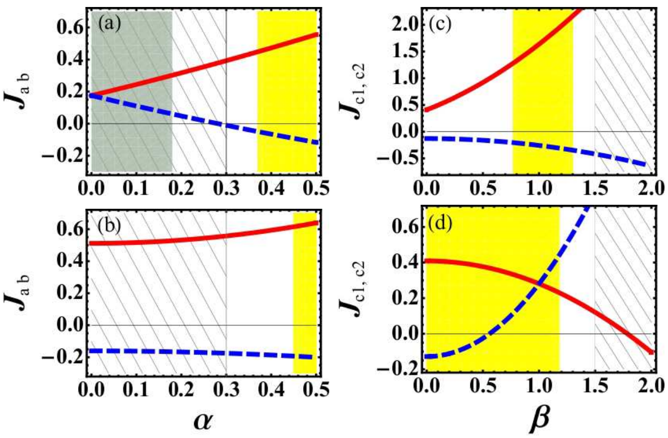

Fig. 3: (Colour on-line) Spin exchange constants for different hoppings $\{\alpha, \beta\}$: (a,b) J_{ab} for increasing α, and (c,d) J_{c1} and J_{c2} for increasing β; solid (dashed) lines depict J_γ calculated for FO (AO) order. Panels (a,c) and (b,d) for T^x and T^z pseudospin order. Areas with oblique lines depict realistic values values of α and β in $R\mathrm{O}_2$ (see also main text). In shaded areas orbital order is stable for the realistic value of $\beta \in [1.5, 2.0]$ (left panel) and $\alpha \in [0.0, 0.3]$ (right panel): gray (yellow) — C-AO order stable; dark gray (green) — FO order stable.

'wrong' signs of exchange constants) and GKR are violated in at least one plane (see also footnote [3]). The resulting imaginary energies (soft modes) indicate that the ground state is unstable. Physically, this is related to the dispersive character of the spin waves, i.e., a propagating spin-flip excitation is not balanced by an "Ising-like" local excitation and the ground state collapses.

The above can also be seen in the critical case ($\omega_{\mathbf{k}} = 0$) when $A_{\mathbf{k}}^2 = B_{\mathbf{k}}^2$ in parts of the Brillouin zone (this happens if $J_{ab} = J_{c1} = J_{c2} > 0$ or $J_{ab} = J_{c1} = -J_{c2} < 0$). Although then the energies $\omega_{\mathbf{k}}$ remain real, the quantum corrections to the order parameter in the harmonic approximation $\delta S = \sum_{\mathbf{k}} (A_{\mathbf{k}} - \omega_{\mathbf{k}})/(2N\omega_{\mathbf{k}})$ diverge [4] due to the onset of soft modes and the classical order is destroyed, cf. Ref. [6].

After establishing the importance of having the 'correct' sign for all magnetic exchange constants, we now discuss them more explicitly for five orbital states: (i) C-AOx [Fig. 2(c)] and FOx (not shown) states with ordered T^x pseudospin, (ii) C-AOz [Fig. 1(b)] and FOz [Fig. 2(d)] states with uniform T^z order, and (iii) an orbital liquid (OL) state with disordered orbitals. Note that, as usual [2], the C-AO order means twice as many bonds with AO order (ab plane and one of the c planes) than the FO order (other c plane), though, the choice of FO directions is different than for C-AF order. The latter order generates a minimal number of bonds with 'wrong signs' in a wide parameter range of α and β, see Fig. 3. We begin with spin exchange constants for C-AOx and FOz phases. Since the GKR are here perfectly fulfilled for almost all values of α and β, one immediately notices that always at least one of the exchange constants will have a 'wrong' sign. Besides, also the magnitudes of the exchange constants with 'wrong' signs are such that for realistic values of β and α (see meshed areas in Fig. 3), the C-AF cannot be stable for C-AOx or FOz order. Finally, even if for some values of α and β the GKR are not enforced by the Hamiltonian for these two orbital states, this only *increases* the number of exchange constants with 'wrong' signs. Similarly, also for the OL state (not shown) the C-AF phase is unstable in the entire range of η.

A different situation, however, arises for the C-AOz and FOx states. Here, the C-AF phase can be stable for a wide parameter range of α and β (including the values realized in $R\mathrm{O}_2$). On one hand, for the FOx case this is purely due to the fact that the spin exchange with the 'wrong' sign in the ab plane has typically a much smaller magnitude than the AF one in c planes, see Figs. 3(a) and 3(c). On the other hand, for the C-AOz state this is not only due to the fact that the 'wrong' exchange constants have small magnitude but rather because the GKR are not enforced here and the signs of the spin exchange constants permit a stable C-AF phase in the LSWT, see Figs. 3(b) and 3(d). More precisely, for a wide range of β the spin exchange constant J_γ is positive *both* in the FOz c_1 plane and in the AOz c_2 plane (e.g. $J_\gamma > 0$ still for FO state with $\beta = 1.77$ as realized in RbO_2). There is thus no frustrated magnetic coupling in the AOz state, as a lifting of the classical GKR permits instead that all spin couplings have the correct sign.

Since the spin order can be so easily destabilized by the spin excitations, we have performed a linear orbital-wave theory (cf. Ref. [27]) and verified that soft modes arise *also* in the orbital wave spectrum. It is remarkable that the only two orbital states for which the C-AF was stable with respect to spin waves (the C-AOz and FOx orbital states) collapse now in a very similar way as shown for the spin case in Fig. 2 for almost whole range of realistic values of α and β in $R\mathrm{O}_2$, see shaded areas in Fig. 3. In fact, the FOx state can only be stable for small values of α which may be realistic for some $R\mathrm{O}_2$ compounds, but not for $\alpha = 0.3$ as suggested for RbO_2. This order thus cannot explain the origin of the same C-AF order stable in all $R\mathrm{O}_2$. The physics behind these phenomena is as follows: (i) finite transverse hopping α enhances orbital fluctuations in the ab plane (due to the 'wrong' sign of the orbital interactions for the FO and FM order in the ab plane) which are for the orbital case of comparable size as in the c planes and this destroys the FOx orbital order; (ii) while the interorbital hopping β (discussed below) turns

[3] There is just one exception to this rule: when the spin exchange constant with the 'wrong' sign has a smaller absolute value than the other *two* exchange constants with the 'correct' sign. This means that either (i) $J_{ab} > 0$, $J_{c1} > 0$, $J_{c2} > 0$, if $|J_{ab}| < |J_{c1}|$ *and* $|J_{ab}| < |J_{c2}|$, or (ii) $J_{ab} < 0$, $J_{c1} < 0$, $J_{c2} > 0$, if $|J_{c1}| < |J_{ab}|$ *and* $|J_{c1}| < |J_{c2}|$ (and similar for $J_{c1} \leftrightarrow J_{c2}$).

[4] N is the number of lattice sites. When $J_{ab} = J_{c1} = J_{c2} > 0$, then $\delta S \sim \int \mathrm{d}k_x \mathrm{d}k_y \mathrm{d}k_z \frac{1}{k_z}$, while when $J_{ab} = J_{c1} = -J_{c2} < 0$, then $\delta S \sim \int \mathrm{d}k_x \mathrm{d}k_y \mathrm{d}k_z \{(k_x^2 + k_y^2)/(k_x + k_y)\}$. In both cases $\delta S \to \infty$.

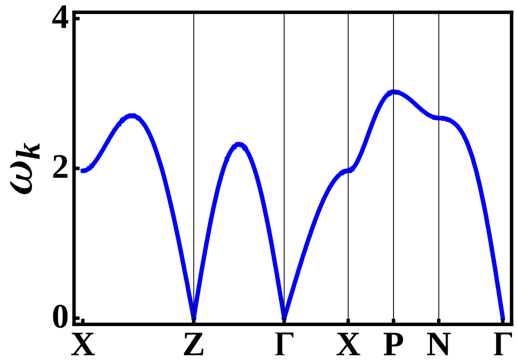

Fig. 4: (Colour on-line) Spin-wave dispersion $\omega_{\mathbf{k}}$ along the high symmetry directions in the Brillouin zone for the C-AOz phase using Eq. (9). Parameters: $\alpha = 0.30$ and $\beta = 1.77$ [19]. High symmetry points: $X = (\pi, 0, \pi)$, $Z = (0, 0, 2\pi)$, $\Gamma = (0, 0, 0)$, $P = (\pi, \pi, \pi)$, $N = (\pi, 0, \pi)$ cf. Ref. [16] with $a \equiv c \equiv 1$.

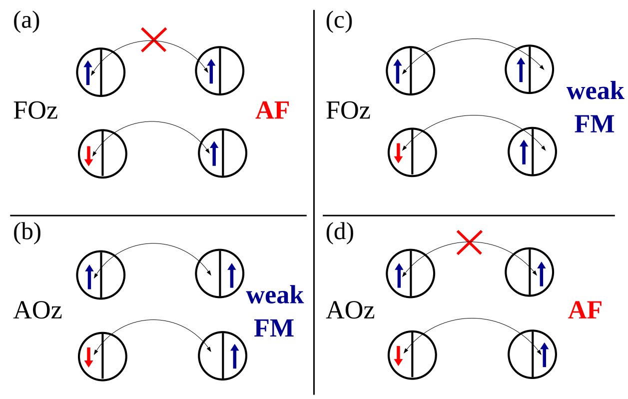

Fig. 5: (Colour on-line) Artist's view of the FOz and AOz states with: (a-b) diagonal t_{xx} hopping not violating the GKR; (c-d) interorbital t_{xy} hopping fully violating the GKR. Weak FM exchange in (b) and (c) follows from finite $\eta > 0$.

out to be a crucial ingredient in stabilizing the observed magnetic order *provided* the orbital sector shows C-AOz order, precisely this interorbital process suppresses the C-AOz order.

However, the orbital order is also sensitive to the orbital-lattice coupling, stemming from the JT effect, and the resulting orbital state $|\phi\rangle$ determines spin-wave dispersion (see below and Fig. 4). In fact, a standard and rather weak JT interaction is enough to stabilize C-AOz order [cf. Fig. 1(b)] over the OL phase for realistic values of α and β. We have verified that the interaction,

$$\mathcal{H}_{\rm JT} = E_{\rm JT} \sum_{\langle \mathbf{ij}\rangle || ab} T^z_{\mathbf{i}} T^z_{\mathbf{j}}, \qquad (10)$$

with $E_{\rm JT} \simeq 0.9$ ($\simeq 12$ meV for realistic $J_\sigma \simeq 13$ meV in KO_2 [16]) is enough to overcome the orbital interactions that follow from the spin-orbital superexchange Eq. (1) (an even smaller $E_{\rm JT} \simeq 0.04$, i.e., $\simeq 0.1$ meV suffices for RbO_2 with $J_\sigma \simeq 3.3$ meV [19]). Furthermore, recently precisely this type of robust JT-induced AO order of T^z pseudospins was identified [compare present Fig. 1(b) with Fig. 3(c) of Ref. [18]]. The estimated JT interaction at 22 meV per formula unit is well above the minimal value of $E_{\rm JT}$. Since the invoked mechanism relies merely on electrostatic repulsion between electrons on alkali and oxygen atoms in bct lattice, we suggest that it is universal for all alkali RO_2 hyperoxides.

After explaining how the spin and concomitant orbital order can both be stable on the frustrated bct lattice, we now present the spin-wave dispersion Eq. (9) in the C-AF phase with C-AOz order [Fig. 1(b)] as imposed by the JT effect. Now all magnetic couplings have a sign compatible with the existing magnetic order, see the discussion above, and the spin-wave dispersion (Fig. 4) has no soft modes and indicates that the ground state is stable. The spin-wave dispersion could be verified by future experiments.

Remarkably, the C-AOz order supports spin-exchange constants that are AF for FOz bonds along c_1 as well as for AOz bonds along c_2 and this explains the origin of stable C-AF spin order in RbO_2 [$\beta = 1.77$ and $J_\gamma > 0$ for FO and AO state in the c planes, see Fig. 3(d)]. Besides, it is very plausible that also in KO_2 the C-AF phase is stable not because the magnitudes of the exchange constants with 'wrong' signs are small but because both exchange constants in c planes are positive; we have verified that a slightly smaller $J_H = 0.4$ eV as suggested in Ref. [18] for KO_2 (and $\beta = 1.9$) yields $J_\gamma > 0$ for FO state in the c plane. Altogether, this suggests that the classical GKR, see Figs. 5(a) and 5(b), are not enforced in the RO_2 family and this resolves the puzzle of stable C-AF phase.

Therefore, let us now try to understand the origin of this *generalization* of the GKR by studying Hamiltonian (1) in one of the c planes only. If hoppings were almost only interorbital, i.e., $\beta \gg 1$, the GKR would simply be inverted and bonds with FOz (AOz) order would drive FM (AF) couplings, see Figs. 5(c) and 5(d). If both inter- and intra-orbital hopping contribute, the two opposing tendencies compete and the magnetic exchange is tuned by them. For a broad range of intermediate values of β, AF interactions are established both on the FOz bonds (driven by orbital-conserving J_{xx}) and on the AOz bonds (driven by interorbital $\beta^2 J_{xx}$), see Fig. 5(a,d). The AF coupling dominates, because antiferromagnetism, which is due to the Pauli principle, is much stronger than ferromagnetism, which is caused by the energy difference $\propto \eta$ between triplet and singlet intermediate states of the superexchange processes.

The JT effect is crucial for this generalization of the GKR — without it large interorbital hopping t_{xy} orders the T^x pseudospin component instead of the T^z component in the single c plane under consideration. It becomes then more natural to consider the basis of T^x eigenstates,

being $\{(p_x+p_y)/\sqrt{2},(p_x-p_y)/\sqrt{2}\}$. In this rotated basis, the full hopping term (consisting of t_{xy} and t_{xx}) is diagonal, while 'interorbital' hopping vanishes. Classical GKR are then fulfilled, and spin exchanges are positive (negative) for FOx (AOx) states in the c plane.

Note that such generalized GKR can arise whenever the orbital order on a bond is not solely stabilized by the same spin-orbital superexchange Hamiltonian that determines the spin exchange interaction. On a geometrically frustrated lattice, another route to this behaviour can occur when the ordered orbital component preferred by superexchange depends on the direction *and* the relative strengths fulfill certain criteria. In the bct case discussed here, hoppings within the ab plane are diagonal in the $\{p_x,p_y\}$ basis, while hoppings along the c_1 and c_2 planes are diagonal in the $\{(p_x+p_y)/\sqrt{2},(p_x-p_y)/\sqrt{2}\}$ basis. Since the c_1 and c_2 bonds frustrate each other as long as the traditional GKR hold (see above), it follows that the C-AF order can be stable on the bct lattice only if the orbital order is the one preferred by the ab plane. This appears to be somewhat counterintuitive, as there is only one ab plane and two c_1 and c_2 planes — it requires either a JT effect (as here) or ab hoppings that are considerably stronger than those along c_1 and c_2. This second scenario is not expected for realistic parameters of $R\mathrm{O}_2$ but in principle could also be possible in a frustrated lattice. For instance, it might play a role for d orbitals with t_{2g} symmetry on a triangular lattice, where hopping is strongly anisotropic and 'interorbital' along all bonds, so that — at least some — orbital interactions are always frustrated [28].

We have shown that the onset of the AF order on the frustrated bct lattice in $R\mathrm{O}_2$ systems requires a generalization of the well-known Goodenough-Kanamori rules, because ordered states that obey these classical rules are destabilized by spin and orbital waves. A generalization arises in the presence of large interorbital hopping whenever the orbital order enforced by Jahn-Teller coupling is qualitatively different from the one favoured by orbital superexchange. We emphasize that to the best of our knowledge, there exists no alternative explanation of the origin of the C-AF order in this class of compounds on the *frustrated* bct lattice. For instance, a recent study using the spin-orbital model at $\eta=0$ (see footnote [5]) starts from the assumption of C-AF order [19]. Furthermore, neither the spin-orbit coupling suggested in Ref. [16] to explain the high temperature behaviour of KO_2 nor the indirect kinetic exchange interaction can explain the onset of the FM planes in the $R\mathrm{O}_2$ hyperoxides (see footnote [6]).

Summarizing, alkali $R\mathrm{O}_2$ hyperoxides are different from both 'plain vanilla' p-orbital systems in optical lattices with effective interactions of purely electronic origin, and from d-orbital compounds like the manganites. In the latter case the superexchange and Jahn-Teller coupling support the same orbital order and the standard Goodenough-Kanamori rules are perfectly obeyed [29].

[5] For $\eta=0$, spin exchange vanishes in ab planes for the considered p orbital order, similar to ab planes in the e_g compound KCuF_3 [6].

[6] Although a weak tendency toward FM order has been found (within generalized gradient approximation [17]) in KO_2, the crucial dependence on the type of tilting of O_2 molecules suggests that this is not a generic mechanism capable of explaining the C-AF order in all alkali hyperoxides with different types of distortions [1].

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